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(54) **Title:** DIGITAL PRINTING INK COMPOSITION

(57) **Abstract:** A digital printing ink composition comprises at least a glass frit or metal particles having a particle size less than 2 μm and a dispersion medium, preferably comprising also an inorganic pigment, and is suitable for deposition onto substrates. The printed ink coating can be fired to yield a permanent coating.

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DIGITAL PRINTING INK COMPOSITION

This invention relates to a composition suitable for application by an ink-jet print head, to a method of producing such a composition and its use for the coating of substrates.

There are many advantages of using ink jet printing as a printing or coating technique. It can produce high quality prints at high speed. As a non-contact method, it can be used to print on a wide range of substrates having different surface textures. The image to be printed is stored digitally, thus obviating the need for screens, engraving etc. In addition, images can be altered easily and rapidly, thus allowing for more variation in prints. No down time or cleaning between different designs is required. As the ink is only deposited where required, the technique minimises ink wastage and reduces cleaning requirements. The small size of the nozzles in a typical ink-jet print head place stringent demands on the physico-chemical properties of any ink used, however. Factors such as pigment particle size and ink viscosity, and the quality of pigment and frit dispersion, are important to prevent nozzle blockage.

Compositions for application to substrates such as ceramics and glasses commonly include a powdered glass component or 'frit'. During subsequent heat treatment ("firing") the frit melts and bonds to the substrate. Typically, the composition also contains an inorganic pigment, which does not itself melt during heat treatment, but is affixed to the substrate by, or incorporated with, the frit. A combination of a frit and a pigment is often termed an enamel. Enamels are widely used to decorate or produce coatings on ceramics such as tableware, where the composition may be applied by simple screen-printing methods, by applying decals comprising the enamels or by manual application for example, using dipping or a brush. The properties of compositions applied by such techniques can vary within wide ranges without significantly affecting the final coating. Compositions which do not contain a frit can only be affixed to substrates which at least partially melt during heat treatment, such as those already coated with a frit-containing composition, or by applying an over-layer of a frit-containing composition.

It is well known to use organic pigments in ink-jet ink formulations. These are soft materials and are available with a small particle size, in the order of tens to hundreds of

nanometres. Such formulations are widely used for printing onto paper. It is less well known to use formulations containing harder, inorganic pigments. WO 98/51749 discusses ink-jet compositions with low sedimentation rates, containing pigments of particle size less than 300 nm. Patent GB 2268505 discusses continuous ink-jet printing of inks containing pigments of a size 0.2 – 2.0 μm. The pigments are suspended in a solvent, such as MEK and printed onto ceramic or glass substrates prior to firing. US 6,332,943, discuss formulations containing organic and/or inorganic pigments stabilised with particular dispersants. US 6,110,266 describes pigment preparations containing particles of inorganic materials of particles size 0.1-50 nm. There is little or no discussion of practicable ink-jet inks containing a frit component or metal particles, and we do not believe that such inks have been successfully prepared and printed.

A frit may be defined as "any fused substance or mixture quenched to a glass-like form" and is thus an amorphous material, as opposed to inorganic pigments which are very often crystalline and thus possess a primary particle size. Frits are also generally harder materials than inorganic pigments and as such, there is a danger that they could abrade the nozzles of an ink-jet printer. The other concern with frit (and indeed inorganic pigments) is that they are dense materials. Compared to organic pigments which have densities of the order of 1 g cm^{-3}, frits have densities in the order of 2-5 g cm^{-3}. This means that compositions containing them may segregate more rapidly than conventional ink-jet inks. The properties of brittleness, hardness and high density combine to make frit a highly difficult material to formulate into an ink suitable for ink-jet printing. Similar problems apply to metal particles.

The present invention provides an improved composition which can be applied to a substrate by digital printing techniques and fixed thereto by heat treatment. Although the prime interest of the Applicants is in inks formulated for ink-jet printing, successful trials have been carried out in producing inks according to the invention which have been successfully printed by bubble jet techniques, and it is contemplated that inks according to the invention will be suitable for other digital printing systems using liquid, thermoplastic or solid inks. The skilled person will determine necessary characteristics such as viscosity, drying characteristics etc.

In accordance with a first aspect of the present invention, a digital printing ink composition, for example suitable for application by an ink-jet print head, comprises particles of

at least one glass frit or metal, wherein the particles have a d_{100} size less than 2μm, preferably less than 1 μm, more especially less than 0.7μm, and a dispersion medium.

It is to be understood that the composition may be a concentrate, to be diluted before use, possibly with the addition of additional components, for application by an ink-jet printing head or by other systems.

The glass frit may be any suitable glass frit, for example a bismuth silicate frit, zinc borosilicate frit, lead silicate frits or other suitable frits. Mixtures of two or more glass frits are also suitable. In general, the particular frit chosen will depend upon the substrate and the firing profile, as is conventional.

Preferably, the at least one glass frit or metal particles comprises between 1 and 70wt%, more preferably, between 20 and 50wt% of the composition.

For some applications it may be desirable to apply a coating of glass frit, or a blend of glass frits or a blend of one or more glass frits with one or more colourless additives such as silica or alumina only, from a frit/dispersion medium ink. This may be to provide a transparent or hazy coating to a substrate; a desired texture possibly using a relatively harder frit with a relatively softer frit, which textured print may be overprinted or gilded (so-called "etch imitation", for example using Johnson Matthey BRF 900 or AF 2900, and in the case of etch imitation printing, a thinner print is generally desirable, so that the solids content of the ink as printed isles than 45 wt%, preferably less than 30 wt%) or perhaps a covert security marking. Preferably however, the composition further comprises at least one inorganic pigment. Suitable pigments will be known to those skilled in the art, are commercially available and include any refractory pigment. Some non-limiting examples include copper chromite as a black, cobalt aluminium oxide and nickel chromium oxide. The pigment may be simply a coloured frit, such as a blue frit, for example Johnson Matthey blue frit GK277B, and the invention thus encompasses such a coloured frit as the sole colouring agent in an ink composition, or in addition to a separate pigment. Frit and pigment may be combined in the form of an enamel, that is a sintered combination of frit and pigment. Further the ink composition may comprise a pigment, or conceivably a frit or frit component, that is fluorescent or luminescent. Such pigments

include: magnesium fluorogermanate red (Meldform Germanium Ltd), Lumilux green CD117, Lumilux blue CD164, Lumilux red CD115 and Lumilux yellow/orange CD130 (All Lumilux products available from Allied Signal or its distributors, e.g. Chemproha, Chemie Partner BV).

Mixtures of two or more pigments, or pigments with metal particles are also suitable.

Preferably, the at least one inorganic pigment comprises between 1 and 40wt% of the composition.

In order to prevent blockage of ink-jet print heads the particle size of the glass frit or metal particles, as well as any pigment used should be small. Preferably, the at least one glass frit and any pigment used have a d_{100} particle size of less than 2 μm, more preferably less than 1 μm, most especially less than 0.5 μm. As is known in the art, d_{100} particle size is the particle size at which 100% of particles in a given sample are smaller, and may readily be achieved by sieving out oversize particles.

A wide range of dispersion media may be used. Factors influencing the choice of medium include solvent viscosity, evaporation rate, surface tension, odour and toxicity. Suitably, the medium comprises one or more of water, alcohols, glycol ethers, lactates, glycol ether acetates, aldehydes, ketones, aromatic hydrocarbons and oils. Mixtures of two or more solvents are also suitable. Some presently preferred examples include; diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether and 1-methoxy 2-propanol. These media are ideal for "drop-on-demand" piezoelectric or electrostatic printheads.

The composition may further comprises one or more synthetic or natural polymers. Polymers may be used to alter the viscosity and viscoelastic nature of the compositions which influences the break-up of the jet and thus ink satellites and ligaments. Polymers may also be used to provide green strength to the applied composition prior to heat treatment. Suitable polymers include; poly(acrylates), poly(methacrylates), cellulose derivatives, poly(styrene-co-maleic anhydride) polymers both partially esterified and non-esterified, poly(vinylpyrrolidone), poly(styrenes), poly(vinylalcohols), poly(vinylbutyral) and poly(esters).

Rosin-derived material such as hydrogenated rosins, rosin dimers, maleated rosin and rosin esters, may also be added.

The composition may further comprise one or more additives. These may include surfactants to modify the surface tension or wetting properties of the ink such as poly(siloxane) based wetting agents, defoamers, humectants, biocides, buffers, adhesion promoters, tackifiers and dyes. The additives may also comprise "dispersing aids", such as, but not limited to those from the disperBYK, Solsperse or Dispex ranges, in particular Disperbyk 180 and Solsperse 40000, and/or rheology modifiers.

In accordance with a second aspect of the present invention, a method for producing a composition, according to the invention, such as suitable for application using an ink-jet print head, comprises forming a dispersion of a glass frit in a dispersion medium, comminuting the dispersion to reduce the particle size of the frit, and filtering the dispersion to remove oversized frit particles. In the case of metal particles, techniques are known for producing small particles by solution chemistry and other techniques.

In the case of frit/pigment combinations, the method further comprises forming a second dispersion of an inorganic pigment in a solvent, comminuting the dispersion to reduce the particle size of the inorganic pigment, filtering the second dispersion to remove oversized pigment particles, and combining the filtered second dispersion with the filtered frit dispersion. Alternatively, both the frit and the pigment may be comminuted as a single dispersion, which is then filtered. This leads to a simpler process but is presently not preferred as the different physical properties of the frit and the pigment make achieving a uniform particle size for both problematic.

One or more polymers, rosin derived materials and/or other additives may be added to the composition prior to, during or after the comminution and filtering steps.

In accordance with a third aspect of the present invention, a method of producing a coating on a substrate comprises applying a composition as described hereinbefore to a substrate using a digital print technique such as an ink-jet printing head, and heat treating the substrate. In

a variant, the substrate is a transfer medium, such as a gum or release paper, and the printed pattern in the form of a decal is transferred to the substrate before firing.

The substrate may be a ceramic such as bone china, porcelain or earthenware, a glass article or sheet or a metal, or similar substrate such an enamelled metal substrate or a glazed substrate such as a tile. The substrate may be a plastics substrate, for example a glass fibre-reinforced printed circuit board substrate, in which case the heat treatment may be a temperature- or UV-initiated curing step.

The temperature and length of the heat treatment step will depend on the nature of the composition applied and the type of substrate. Typically, temperatures between 400 and 1300°C will be suitable. Heat treatment may be by any suitable means for example, furnace heating, laser heating. The heat treatment conditions can be optimised by routine trial and error.

The coating may be a decorative coating such as a picture or pattern. Alternatively, the method may be used to provide a functional coating. Some examples of functional coatings include security markings, including information tagging or information marking and barcodes, and, coatings on glass sheets to provide safety contrast bands to indicate the presence of glass sheets to pedestrians, barrier coatings or bands including UV barrier coatings, such as black obscuration bands for vehicle glass. In the case of metal inks, such as gold or silver, functional coatings such as conductive tracks may be produced, or a decorative coating in the case of gold. Gold particle-containing inks may also comprise solubilised gold compounds which yield a gold film.

The invention will now be described by way of example only. The skilled person will readily understand how to use the disclosure of this description and examples to produce all aspects of the present invention.

Example 1

A bismuth silicate glass frit J5405F (440g, Johnson Matthey Glass, Maastricht) supplied with a d_{90} of 15 microns, was stirred into a mixture of Dowanol DB (145g),

poly(vinylpyrrolidone) (6g) and Disperbyk 180 (11g). The mixture was dispersed in a Dispermat bead mill at a rate of 5000 rpm for 6 hours. The milling media used was 0.8mm yttria stabilised zirconia beads. The particle size attained was a d_{90} of <2 microns. A further 50g of Dowanol DB was used to clear the ink from the mill and then the mixture was further diluted with the addition of more medium to give a solids content of 49.3% by weight.

Example 2

A copper chromite pigment (280g) supplied with a d_{90} of 3.1 microns, was stirred into a mixture of Dowanol DB (108g), poly(vinylpyrrolidone) (4g) and Disperbyk 180 (9g). The mixture was dispersed in a Dispermat bead mill at a rate of 6000 rpm for 1 hour to attain a particle size with d_{90} <1.5 microns. The milling media used was 0.8mm yttria stabilised zirconia beads. A further 50g of Dowanol DB was used to clear the ink from the mill. The solids content was 61%.

Example 3

Dispersions as made in Examples 1 and 2 were filtered through a 3 micron polypropylene precision mesh in order to remove any larger particles. The two dispersions were mixed together thoroughly at the ratio of 3 parts frit to 1 part pigment by weight to produce a black ink. The ink had a viscosity of 9 mPas at a shear rate of $10s^{-1}$ as measured on a Bohlin CVOR rheometer at 23°C. The surface tension was 30.1 mNm^{-1} as measured on a Camtel CDA 100.

Example 4

Ink prepared as in Example 3 was printed through a Trident Ultrajet II piezoelectric print head onto glass. The prints were further treated by heating in a furnace with a 10 minute ramp from room temperature to 700°C followed by a dwell at 700°C for 3 minutes and a return to room temperature over 10 minutes. The ink was well adhered to the glass and possessed a good opacity.

Example 5

A lead borosilicate frit 2160BF (440 g, Johnson Matthey Glass), supplied with a d_{90} of 1.9 microns, was stirred into a mixture of Dowanol DB (165 g) and Solsperse 40000 (11 g). The mixture was dispersed in a Dispermat bead mill at a rate of 6000 rpm for 6 hours to obtain a particle size with d_{90} of less than 1.5 microns. The milling media used was 0.8 mm yttria stabilised zirconia beads. The ink was removed from the mill and diluted to 50 weight % solids using Dowanol DB. The residue ink remaining in the mill was removed separately and not added to the main ink.

Example 6

A blue cobalt aluminate pigment (420 g), supplied with a d_{90} of 1.9 microns, was stirred into a mixture of Dowanol DB (216 g), poly(vinylpyrrolidone) (8 g) and Disperbyk 180 (18 g). The mixture was dispersed in a Dispermat bead mill at a rate of 5500 rpm for 2 hours to obtain a particle size with d_{90} of 1.1 microns. The milling media used was 0.8 mm yttria stabilised zirconia beads. The ink was removed from the mill and diluted to 50 weight % solids using Dowanol DB. The residue ink remaining in the mill was removed separately and not added to the main ink.

Example 7

Ink prepared as in example 3 was printed through a Spectra piezoelectric printhead. The prints were further treated by heating in a furnace to 580 °C. The ink was well adhered to the glass and possessed a good opacity.

Example 8

A bismuth silicate glass frit J5405F (35.6 kg, Johnson Matthey Glass) supplied with a d_{90} of 1 5 microns was stirred into a mixture of Dowanol DB (13.54 kg) and Disperbyk 180 (0.864 kg). The mixture was dispersed and milled on a Netzsch LMZ 10 for 8 hours. After 6 hours a further 2.66 kg of Dowanol DB/Disperbyk mixture (ratio 94 parts :6 parts) was added. The milling media used was 0.4-0.7 mm zirconox beads. The particle size obtained was a $d_{90} < 1.5$ microns. This 'inkjet concentrate' had a viscosity of 320 mPas at a shear stress of 50 Pa after an initial pre

shear of 20 seconds at 50 Pa. The 'inkjet concentrate' was diluted with a glycol ether or glycol ether acetate to attain a viscosity < 15 mPas required for inkjet printing through Spectra or Trident printheads. Typical solids content was 40 – 55%

Example 9

A copper chromite pigment (25 kg) supplied with a d_{90} of 3.1 microns was stirred into a mixture of Dowanol DB (9.5 kg) and Disperbyk 180 (0.625 kg). The mixture was dispersed and milled on a Netzsch LMZ 10 for 5 hours. After 3 hours a further 2.66 kg of Dowanol DB/Disperbyk mixture (ratio 94 parts :6 parts) was added. The milling media used was 0.4-0.7 mm zirconox beads. The particle size obtained was a d_{99} < 1.0 microns. The 'inkjet concentrate' was diluted with a glycol ether or glycol ether acetate to attain a viscosity < 15 mPas required for inkjet printing through Spectra or Trident printheads. Typical solids content was 40 – 55%

Example 10

The two dispersions made in examples 8 and 9 were mixed together in a ratio of between 66% frit : 34% pigment to 75% frit : 25% pigment. This enamel dispersion for inkjet has a viscosity < 15 mPas and a surface tension < 35 mNm^{-1}. The mixed dispersion was printed through a Spectra head.

Example 11

A Johnson Matthey frit (J5405F) was milled in Dowanol DB together with 0.46 wt% Disperbyk 180 to produce a first suspension. A conventional copper chromite black pigment (Black 1G, Shepherd Color Co.) was milled in Dowanol DB, together with 2 wt% of Disperbyk 180, and mixed with the first suspension in an amount to yield a frit to pigment solids ratio of 3:1. The mixed suspensions are diluted with Dowanol PMA and the other components listed below, and stirred for an hour using a high shear mixer. The mixture was filtered through a 1 micron screen, and the viscosity adjusted to about 15 cP, to form an ink. The ink was successfully printed onto glass sheet using a commercial ink-jet print head, and the glass sheet was fired.

Components (by weight):

36.0% frit solids
12.0% pigment solids
15.3% Dowanol PMA (Dow Chemical)
33.5% Dowanol DB (Dow Chemical)
0.9% Neocryl B842 polyacrylate (Neo Resins)
1.5% DisperByk 180 (Byk Chemie)
0.8 % Byk 358 (Byk Chemie)

Example 12

A solution of silver nitrate (12.5 g – 25.0 g) in deionised water was prepared. This was added to a 2-10 wt% polyvinylpyrrolidone (Mol. Wt. 40,000 or 55,000) solution in Dowanol DE, Dowanol TM or a 50:50 mix of Dowanol PM and diethyleneglycol (50g). The solution was gently stiired for 24 hours to form a PVP-stabilised silver nanoparticle suspension. To 40g of this suspension up to 0.1 g of rhodium acetate was added as an adhesion improvement component. The inks produced have been successfully printed through Spectra and Trident printheads.

Example 13

27.6 g gold t-butyl thiophenol nanoparticles (prepared according to Johnson Matthey EP 1272464 was mixed with a solvent (a glycol ether, such as dipropyleneglycol monopropyl ether (Dowanol DPnP), dipropyleneglycol monobutyl ether (Dowanol DPnB) or diethyleneglycol monobutyl ether (Dowanol DB), or a ketone such as 3,3,5 trimythylcyclohexanone or menthone.) After stirring, the resulting gold particle suspension is filtered through a 1 micron filter mesh. The suspension may contain additional components selected from one or more of rhodium ethylhexanoate for promotion of gold film formation, polyvinylpyrrolidone (MW 40,000) as a film former (preferably ininitially dissoled in the solvent) and a vanadium salt to

improve adhesion. After adjustment of viscosity to less than 30 mPas, if necessary, the resulting gold ink was successfully printed through a Spectra or Trident piezoelectric drop-on-demand printhead.

CLAIMS

1. A digital printing ink composition comprising particles of at least one glass frit or metal, said particles having a particle size less than 2 μm, and a dispersion medium.

2. A composition according to claim 1, wherein the at least one glass frit or metal particles comprises between 10 and 70wt%, preferably between 20 and 50wt% of the composition.

3. A composition according to claim 1 or 2, further comprising at least one inorganic pigment.

4. A composition according to claim 1 or 2, further comprising a colourless refractory material.

5. A composition according to any one of the preceding claims, having a total solids content of at least 45 wt%, preferably at least 50 wt%.

6. A composition according to claim 3 or claim 5 as dependent upon claim 3, wherein the at least one inorganic pigment comprises between 1 and 40wt% of the composition.

7. A composition according to any one of claims 3 or 5 as dependent upon claim 3, or claim 6, wherein the pigment is a black pigment, preferably copper chromite.

8. A composition according to any preceding claim, comprising at least one glass frit having a d_{100} particle size of less than 1.5 μm, more preferably less than 1 μm.

9. A composition according to any of the preceding claims and containing an inorganic pigment, wherein the inorganic pigment has a d_{100} particle size of less than 2 μm, preferably less than 1 μm.

10. A composition according to any preceding claim, wherein the dispersion medium comprises one or more of water, alcohols, glycol ethers, lactates, glycol ether acetates, aldehydes, ketones, aromatic hydrocarbons and oils.

11. A composition according to any preceding claim further comprising one or more polymers chosen from: poly(acrylates), poly(methacrylates), cellulose derivatives, poly(styrene-co-maleic anhydride) polymers both partially esterified and non-esterified, poly(vinylpyrrolidone), poly(styrenes), poly(vinylalcohols), poly(vinylbutyral) and poly(esters).

12. A composition according to any preceding claim further comprising a rosin derived material such as hydrogenated rosins, rosin dimers, maleated rosin and rosin esters.

13. A composition according to any preceding claim further comprising one or more additives chosen from: film-forming polymers, dispersing agents, surfactants, rheology modifiers, defoamers, humectants, biocides, buffers, adhesion promoters, tackifiers and dyes.

14. A composition according to any preceding claim and containing metal particles, wherein the metal particles are gold or silver nanoparticles.

15. A composition according to claim 1 or 4, containing no pigment and in the form of an etch imitation ink.

16. A composition according to any one of the preceding claims in the form of an ink concentrate.

17. A method for producing a composition according to any of the preceding claims and comprising a frit, the method comprising forming a dispersion of a glass frit in a dispersion medium, comminuting the dispersion to reduce the particle size of the frit, and filtering the dispersion to remove oversized frit particles.

18. A method according to claim 17, further comprising forming a second dispersion of an inorganic pigment in a solvent or dispersion medium, comminuting the second dispersion to

reduce the particle size of the inorganic pigment, filtering the second dispersion to remove oversized pigment particles, and combining the filtered second dispersion with the filtered frit dispersion.

19. A method according to claim 18, wherein the first and second dispersion have approximately the same particle sizes.

20. A method according to claim 17, 18 or 19, wherein one or more polymers, rosin derived materials and/or additives is added to the composition prior to, during or after the comminution and filtering steps.

21. A method of producing a coating on a substrate, the method comprising applying a composition according to any of claims 1 to 16 to a substrate using a digital printing head, and heat treating the substrate or curing the deposited coating.

22. A method according to claim 21, wherein the substrate is one of a ceramic, a glass or a metal.

23. A method according to claim 21 or claim 22, wherein the coating is a decorative coating or a functional coating.

24. A method according to claim 13, wherein the substrate is automotive glass, and the coating is an obscuration coating.

25. A substrate coated using a method according to any of claims 21 to 24.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB2004/004951

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00 C03C8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/089275 A1 (KAWAMURA HIROYUKI ET AL) 15 May 2003 (2003-05-15) paragraph '0073!; claims 1-11 paragraph '0084! paragraph '0086! -----	1-25
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 02, 30 January 1998 (1998-01-30) & JP 09 265833 A (DAINIPPON PRINTING CO LTD), 7 October 1997 (1997-10-07) abstract -----	1-25

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) & JP 11 314936 A (ASAHI GLASS CO LTD), 16 November 1999 (1999-11-16) abstract -----	1-25
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